

# Synthesis and Physical Properties of Several Aliphatic and Alicyclic Hydrocarbons

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The synthesis and purification of four paraffins, three cycloparaffins, six olefins, and five diolefins, and their intermediates are described. These compounds were prepared by standard reactions or modifications thereof, and purified by fractional distillation. Physical properties of the hydrocarbons are presented, and purity data are given for some of them.

## 1. Introduction

At its outset the hydrocarbon research program at the National Bureau of Standards was concerned with compounds of interest as fuel components in high-compression spark-ignition engines. Therefore, the emphasis was upon highly branched paraffin hydrocarbons [8].<sup>3</sup> With the advent of reaction engines, the researches were directed to the syntheses of alicyclic hydrocarbons and the less highly branched aliphatics with various degrees of unsaturation. The work on the acetylenic hydrocarbons is described in a previous paper [12]. The work described herein is the part of this program, sponsored by the National Advisory Committee for Aeronautics, dealing with the syntheses and purification of 4 paraffins, 6 olefins, 5 diolefins, and three alicyclic hydrocarbons.

## 2. Apparatus

### 2.1. Reaction Vessels

Large-scale reactions were carried out in two commercial 50-gal jacketed reaction kettles designed to permit any temperature from 5° to 150° C to be maintained. One of these was stainless steel, the other was glass-lined steel; both are described in a previous publication [8]. In general, preparations of Grignard reagents were carried out in the stainless-steel vessel; the more corrosive reactions, such as acid oxidations, were conducted in the glass-lined one.

For reactions involving liquid ammonia as a solvent (see sec. 4.9 and 4.10), a 10-gal stainless-steel kettle was used. This reactor was jacketed and

insulated with a 6-in. layer of ground cork. There were appropriate facilities for the addition of reagents or observation of reflux. This equipment has been described previously [12].

### 2.2. Hydrogenation Equipment

Commercial rocking autoclaves of 1-, 3-, and 20-liter capacity were used for this work. A commercial nickel-on-kieselguhr catalyst was used, and the hydrogenations were usually carried out at 140° to 180° C and at a maximum pressure of 2,500 lb/in<sup>2</sup>. This equipment is described in a previous publication [8].

### 2.3. Dehydration Equipment

The dehydrator consisted of a 2- by 48-in. stainless-steel tube placed in a furnace made by winding 35 ft of nichrome wire (1 ohm/ft) around a 3.25-ft length of 2-in. pipe. Aluminum-oxide catalyst was contained in the tube and activated by heating for 4 hr at 250° C in a stream of nitrogen. The feed of material to the apparatus was controlled either by a constant-level device made by modification of an automobile carburetor or by means of a commercial siphon pump whose rate could be regulated. Dehydrations in this work were conducted in the vapor phase at 300° to 320° C. Details of the dehydrator have been given previously [11].

### 2.4. Stills

Six stills were used in this work. These have been described previously [8], but for convenience, the salient features of each are given in table 1.

TABLE 1. Distillation columns

Still	Type	Size	Material of construction	Packing	Pot capacity
11.....	Total reflux-variable takeoff.....	240 by 2..... <i>cm</i>	Monel.....	3/32-in. stainless-steel helices made from 0.010-in. wire.	60,000. <i>ml</i>
12.....	do.....	1,500 by 10.....	Galvanized steel.....	3/8-in. unglazed-porcelain raschig rings.....	210,000.
13.....	do.....	1,500 by 10.....	do.....	do.....	210,000.
18.....	Podbielniak Hypercal.....	127 by 2.5.....	Glass.....	Hell-grid.....	250 to 5,000.
19.....	do.....	250 by 2.5.....	do.....	do.....	250 to 5,000.
21.....	Total reflux-variable takeoff.....	120 by 3.5.....	do.....	1/16-in. glass helices.....	22,000.

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<sup>3</sup> Figures in brackets indicate the literature references at the end of this paper.

### 3. Methods and Techniques

#### 3.1. Preparation of Grignard Reagents

The Grignard reagents necessary for the large-scale syntheses in this work (up to 300 moles) were prepared in the 50-gal stainless-steel kettle. The details of the preparation of these reagents have been reported previously [8]. In all cases, these reagents were reacted in place.

#### 3.2. Reductions with Sodium in Liquid Ammonia

For conversion of acetylenic hydrocarbons to olefins, reduction with sodium in liquid ammonia was used; the product obtained was almost exclusively the *trans* isomer [7]. The description of the preparation of several alkynes is given in a previous paper [12], and some of these were used in the present work. The technique used for these reactions is illustrated by the preparation of *trans*-2-hexene from 2-hexyne (see sec. 4.9). In order to minimize the formation of peroxide catalysts, which induce sodium-amide formation, the sodium metal was freshly cut and immediately added to the liquid ammonia.

#### 3.3. Determination of Physical Properties

The properties measured on the compounds prepared included boiling point, freezing point, refractive index, and density. The methods used for the determination of these properties have been reported previously [11]. Where feasible, purities were determined on selected hydrocarbons by mass spectrometry, low-temperature calorimetry [6], or freezing-curve analysis [13]. The low-boiling compounds and some of the unsaturates were sealed under their own vapor pressure [10]. The physical properties measured on the compounds prepared in this work and on their intermediates are listed in table 2, along with purity determinations, where made. When the purities were measured calorimetrically, the triple point and the molar heat of fusion of the substance [6] were also obtained.

### 4. Preparation of Materials

#### 4.1. n-Octane

This paraffin was prepared by hydrogenation of purified 1-octene obtained from a commercial source (see sec. 4.11 for description of the purification of the

TABLE 2. Physical properties of compounds prepared

Compound	Boiling point at 760 mm Hg	Freezing point in air	Density at 20° C	Refractive index at 20° C	Purity <sup>a</sup>
	° C	° C	g/ml	$n_D^{20}$	Mole percent
n-Octane.....	125.668	-56.864	0.70264	1.39770	99.7 FP
3-Methyloctane.....	144.214	b nf	.7205	1.40630	-----
4-Methyloctane.....	142.425	-53.528	.72017	1.40624	-----
4-Ethyloctane.....	163.637	nf	.73811	1.41506	-----
Methylcyclopropane.....	-----	c -177.51	-----	-----	99.30 LTC
Ethylcyclopropane.....	36.2	d -149.60	.6840	1.3788	98.79 LTC
Cyclobutane.....	-----	e -90.59	-----	-----	99.91 LTC
2-Pentene ( <i>cis</i> and <i>trans</i> ).....	36.7	-----	.6545	{ 1.3812 to 1.3823	{ 99.4 MS
<i>trans</i> -2-hexene.....	67.87	-133.07	.67853	1.39351	-----
<i>trans</i> -3-hexene.....	67.15	-114.28	.67718	1.39410	-----
1-Octene.....	121.26	-101.84	.71486	1.40875	99.2 FP
4-Ethyl-2-octene.....	163.5 to 165.0	nf	.7531	1.4300	-----
4-Ethyl-3-octene.....	160 to 162	nf	.7457	1.4242	-----
Propadiene.....	-34.5	f -136.56	-----	-----	99.13 LTC
2,3-Pentadiene.....	48.2	-125.72	.6957	1.4266	-----
1,5-Hexadiene.....	59.46	-----	.69115	1.40386	-----
2-Methyl-1,3-pentadiene.....	75.76	nf	.72391	1.44529	-----
2,5-Dimethyl-1,5-hexadiene.....	114.472	-74.829	.7420	1.4287	-----
2-Pentanol.....	119.3	nf	.8098	1.4065	-----
3-Pentanol.....	115.5	nf	.8207	1.4111	-----
3-Methyl-3-octanol.....	-----	nf	.8331	1.4298	-----
4-Methyl-4-octanol.....	113 (50 mm)	-----	.8284	1.4316	-----
2-Pentanone.....	102.4	-----	.8095	1.3903	-----
1,1-Dicarboethoxycyclobutane.....	226.3	nf	1.0420	1.4351	-----
Cyclobutane carboxylic acid.....	135 to 138 (110 mm)	-7.1	1.0610	1.4430	-----
Cyclobutylbromide.....	107.4	-----	-----	1.4794	-----

<sup>a</sup> FP, purity from freezing-curve analysis [13]; LTC, purity by low-temperature calorimetry [6] (performed by G. T. Furukawa); MS, purity by mass spectrometry (determined by V. H. Dibeler and F. L. Mohler).

<sup>b</sup> nf, nonfreezing, glassy at low temperatures.

<sup>c</sup> Triple point, measured in calorimeter. Molar heat of fusion = 2,800 ± 100 joules.

<sup>d</sup> Triple point, measured in calorimeter. Molar heat of fusion = 5,600 ± 100 joules.

<sup>e</sup> Triple point, measured in calorimeter. Molar heat of fusion = 1,095 ± 50 joules.

<sup>f</sup> Triple point, measured in calorimeter. Molar heat of fusion = 4,400 ± 100 joules.

olefin). Hydrogenation of 4.32 kg of the 1-octene was effected smoothly, and the crude paraffin was percolated through silica gel and distilled through column 18. The center fraction was reserved for measurements of physical constants.

#### 4.2. 3-Methyloctane

This hydrocarbon was prepared by hydrogenation of the olefins resulting from the dehydration of 3-methyl-3-octanol. The carbinol was prepared by the reaction between ethylmagnesium bromide and methyl-*n*-amyl ketone.

Ethylmagnesium bromide was prepared from 7.2 kg (300 g-atoms) of magnesium and 32.7 kg (300 moles) of ethyl bromide as described previously [8]. After preparation of the Grignard reagent, it was found that the stock of 2-heptanone was only 17.1 kg (150 moles) due to partial delivery of an order. This quantity was added to the Grignard reagent. In order to avoid wasting the excess Grignard reagent and to diminish the working hazards, it was decided to add 19.3 kg (150 moles) of 2-ethylhexaldehyde. This compound was chosen because it would yield 4-ethyl-3-octanol, a compound also needed in another synthesis. Because of the difference in molecular weight and structure, it was presumed the two final paraffins or their intermediates could easily be separated.

Six hours were required to effect the total addition, and the mixture was allowed to stand overnight. The reaction mixture was worked up in the usual manner to obtain 68 liters of ether-carbinol solution. The ether was removed from this by distillation on column 21 to leave a carbinol concentrate.

Considerable difficulty was experienced in attempting to distill the carbinol mixture. This was principally due to dehydration. Since the hydrocarbons were the desired products, it was finally decided to dehydrate the mixture of carbinols and separate the resulting olefins.

The carbinol mixture (13.9 kg) was dehydrated over alumina at 300° C during a period of 150 hr. The crude olefin was separated roughly into two fractions on columns 18 and 21. The first fraction, bp 130° to 150° C, consisted principally of 3-methyloctenes, and the second fraction, bp 150° to 170° C, principally of 4-ethyloctenes. The 3-methyloctenes fraction was redistilled to yield 5,760 ml of material boiling 135° to 150° C. The 4-ethyloctenes fraction was redistilled to give 450 ml of material boiling at 135° to 150° C and 4,325 ml of material boiling 150° to 170° C. Material of like boiling points were combined for a total of 6,210 ml (4.62 kg, 36.7 moles) of 3-methyloctenes, bp 135° to 150° C, and 4,325 ml (3.27 kg, 23.4 moles) of 4-ethyloctenes, bp 150° to 170° C. A considerable amount of high boiling residue remained that was not investigated but was probably aldol formed from 2-ethylhexaldehyde.

A charge of the 135° to 150° C cut was refractionated in column 19 in order to obtain samples for physical properties. However, no sharp "plateau"

was obtained; the major portion boiled at 146.5° to 150° C, but the refractive index,  $n_D^{20}$ , rose from 1.4238 to 1.4258.

The mixed 3-methyloctenes (3.5 kg, 28.2 moles) were hydrogenated, and the resulting crude 3-methyloctane (4,000 ml) was distilled in column 19. From this distillation there was obtained 3,160 ml of a 3-methyloctane plateau. A center portion of this had a 20 to 80 percent boiling-point spread of 0.007° C. This was the sample chosen for the determination of the physical constants.

#### 4.3. 4-Methyloctane

This hydrocarbon was prepared by a series of reactions, beginning with the oxidation of 2-pentanol to the corresponding ketone. The 2-pentanone was reacted with *n*-butylmagnesium chloride to yield 4-methyl-3-octanol, which was dehydrated, and the resulting olefins hydrogenated to 4-methyloctane.

Commercial mixed secondary amyl alcohols (190 liters) were fractionated in column 11 to yield 38 liters of 3-pentanol, bp 115.3° to 115.7° C,  $n_D^{20}$  = 1.4104 to 1.4106, and 40 liters of 2-pentanol, bp 119.1° to 119.5° C,  $n_D^{20}$  = 1.4062 to 1.4068.

The 2-pentanol was oxidized, using sulfuric acid-sodium dichromate as the oxidizing agent [15]. Sulfuric acid (13.8 kg) was added with stirring and cooling to 30 liters of water in the glass-lined kettle. To this solution was added 16.5 kg (188 moles) of 2-pentanol, followed by slow addition of a solution of 18.79 kg of sodium dichromate in 37 liters of 4 *N* sulfuric acid. During this addition the solution was stirred and the temperature maintained at 25° to 30° C. After completion of the oxidation step, 56 liters of water was added and the solution steam-distilled until no more organic layer came over. From this operation there was obtained about 19 liters of crude ketone, which was distilled in column 21 to give 15 liters (1.21 kg, 141 moles, 75 percent) of 2-pentanone, bp 103° to 105° C.

*n*-Butylmagnesium chloride was prepared from 13.9 kg (150 moles) of *n*-butyl chloride and 3.65 kg (156 g-atoms) of magnesium in the conventional manner [8]. The addition of the halide required 3 hr, followed by 2 hr of stirring. To this was added 11.8 kg (138 moles) of 2-pentanone over a period of 2½ hr. The reaction mixture was treated in the usual way, and the ether stripped off in column 21. From this reaction there was obtained about 22 liters of crude 4-methyl-4-octanol. This material was distilled in columns 18 and 19, which gave 13.5 kg (93.8 moles, 68 percent) of purified carbinol, bp 105° to 112° C at 50 mm Hg. A sample of the best material was reserved for the measurement of physical constants.

The 4-methyl-4-octanol (13.3 kg, 92.5 moles) was dehydrated by passage over alumina at 300° to 320° C at the rate of 120 to 130 ml/hr. From this step there was obtained 15.6 liters of organic layer and 1.6 liters of water (96 percent dehydration). The olefin was distilled in columns 18 and 19, to yield 10.5

kg (83.4 moles, 90 percent) of mixed 4-methyloctenes, bp 142° to 150° C. A part of the olefin was redistilled in column 19, and almost all the charge distilled over a boiling range of 144.2° to 146.2° C. This was to be expected, because the major olefins would be the very similar *cis*- and *trans*-4-methyl-3-octene and *cis*- and *trans*-4-methyl-4-octene, together with a lesser amount of 2-*n*-butyl-1-pentene. None of the samples taken was considered sufficiently pure to warrant the determinations of physical properties.

A charge of 4.05 kg (32 moles) of the 4-methyloctenes was hydrogenated to give 3.92 kg (30.5 moles, 96 percent) of 4-methyloctane. Four liters of the crude paraffin was distilled in column 18 to recover 2,840 ml of material of suitable purity.

#### 4.4. 4-Ethyl-octane

The synthesis of the olefin precursors of this paraffin (4,325 ml of mixed 4-ethyl-2-octene and 4-ethyl-3-octene) is described in section 4.2. The mixture was redistilled on column 19 to yield two plateaus. The first plateau, bp 160° to 162° C, was tentatively identified as 4-ethyl-3-octene; the second plateau, bp 163.5° to 165° C, was probably *cis*- and *trans*-4-ethyl-2-octene. Physical properties measured on these compounds are listed in table 2. The 4-ethyloctenes were hydrogenated, and the resulting crude paraffin was distilled through still 19 to yield 4-ethyl-octane.

#### 4.5. Methylcyclopropane

This cycloparaffin was prepared by the reaction of zinc with 1,3-dibromobutane, according to the method of Bartleson, Burk, and Lankelma [3]. Several runs were made; a typical preparation is described below.

A mixture of 100 g of water, 196.5 g of zinc dust (3 g-atoms), and 3,000 ml of *n*-propyl alcohol was cooled with an ice-bath. Over a 90-min period there was added 216 g (1.0 mole) of 1,3-dibromobutane to the stirred mixture. The ice-bath was then removed and the flask permitted to warm up. After reaching room temperature, the reaction mixture warmed spontaneously with a brisk evolution of gas, until the flask temperature was 60° to 70° C. When the reaction was completed, the mixture was allowed to cool to room temperature, 250 ml water added, and a stream of nitrogen passed gently through the system for flushing. There collected in the receiver 51 g of product, yield 91 percent. This material was percolated through a silica-gel column kept at -78° C and distilled into a brass bomb for storage. The yield from four such runs totaled 136 g.

#### 4.6. Ethylcyclopropane

This hydrocarbon was prepared by a Wolff-Kishner reduction of the hydrazone of methylcyclopropylketone [1].

To a mixture of 1,285 ml of diethylene glycol, 473.4 g (5.63 moles) of methylcyclopropylketone and 25 ml glacial acetic acid in a 5-liter flask, was added

656 g of 64-percent commercial hydrazine hydrate. The solution was refluxed for about 1 hr and then distilled through a packed column until the head temperature reached 120° C. The residue was cooled and then added dropwise to a mixture (at 180° to 200° C) of 1,350 ml of diethyleneglycol and 420 g sodium hydroxide. The decomposition products were condensed in a trap cooled to -78° C. The crude hydrocarbon was washed successively with water, dilute hydrochloric acid, again with water, and then dried over anhydrous sodium sulfate before distillation in column 19. The distillate boiled 35.5° to 36.5° C and amounted to 152 g, yield 39 percent. This material was redistilled on column 19, and a center cut of 125 ml, bp 35.9° to 36.2° C, was chosen for measurement of physical properties and purity.

#### 4.7. Cyclobutane

Cyclobutane was prepared by a series of reactions that are a modification of the procedure described by Cason and Way [6] and Cason and Allen [5]. In this method, 1,1-dicarbethoxycyclobutane was prepared from diethyl malonate and 1,3-dibromopropane by condensation. The ester was hydrolyzed and decarboxylated by heating with aqueous hydrochloric acid. The silver salt of cyclobutane carboxylic acid was then added to bromine in carbon tetrachloride at -20° C to give cyclobutyl bromide. This was converted to cyclobutane through the Grignard reaction.

(a) *1,1-Dicarbethoxycyclobutane*. To a solution prepared from 13.6 kg (85.0 moles) of diethylmalonate and 4.4 kg of sodium methoxide in 37 liters of absolute alcohol there was added concurrently 13.8 kg (68.5 moles) of 1,3-dibromopropane and a solution of 2.9 kg of sodium methoxide in 25 liters of absolute ethanol. The time of addition was 5½ hr. When the addition was completed, the reaction mixture was refluxed for 45-min, after which the ethanol was removed by distillation. To the cooled residue was added with stirring 26 liters of water and 18 liters of isooctane<sup>4</sup> as solvent. The two layers were separated, and the aqueous layer was stirred again with 7.6 liters of water and 7.6 liters of isooctane. The layers were again separated and the organic layers combined and dried over anhydrous sodium carbonate. The solvent and other low-boiling material were stripped off in columns 18 and 19. The residues were combined and distilled under reduced pressure in column 6. The fraction boiling at 125° to 133° C at 50 mm Hg was collected as 1,1-dicarbethoxycyclobutane. The yield was 7.38 kg (54 percent).

The residue was a very high-boiling material and was not treated further. It probably consisted of 1,1,5,5-tetracarbethoxypentane.

(b) *Cyclobutane carboxylic acid*. The ester was hydrolyzed and decarboxylated in 12 identical runs. In each, a mixture of 900 ml of water, 1,800 ml of concentrated hydrochloric acid, and 600 g (3 moles) of 1,1-dicarbethoxycyclobutane was refluxed until

<sup>4</sup> Isooctane is the trivial name for 2,2,4-trimethylpentane.



the mixture became homogeneous. This took 3 to 4 hr. The water and acid were then distilled, using a short rectifying column. When all the aqueous material was removed, the residue was heated more strongly until the temperature at the head of the column reached 185° C. The evolution of carbon dioxide proceeded smoothly and was complete in less than 1 hr.

The residues from all the runs were combined and distilled in column 18. The portion boiling at 135° to 138° C at 110 mm Hg was collected as cyclobutane carboxylic acid. The yield was 2,681 g (74 percent).

(c) *Cyclobutyl bromide*. This compound was prepared by a series of several similar reactions. Because of its instability, the silver salt was prepared, dried, and reacted with bromine as rapidly as possible.

To a mixture of 200 g (2 moles) of cyclobutane carboxylic acid in 560 ml of water was added with vigorous stirring 2 *N* potassium-hydroxide solution until the solution was faintly basic. To this was added slowly 344 g (2.02 moles) of silver nitrate in 1,100 ml of water. A thick white precipitate of silver cyclobutane carboxylate was obtained. This was stirred for about 1 hr and then filtered. The precipitate was returned to the reaction vessel, stirred with 1,600 ml of water for ½ hr, and again filtered with suction until dry. The final precipitate was washed with methanol, dried by suction again, and then placed in an oven at 100° to 110° C for 24 hr. The silver salt was then cooled in a desiccator over phosphorous pentoxide.

To 2,000 ml of anhydrous carbon tetrachloride cooled to -25° C was added the stoichiometric quantity of bromine for reaction with the silver salt. To this was added the previously prepared silver salt over a period of 1½ to 2 hr, keeping the temperature at -20° to -25° C. The solution was stirred at this temperature for 1 hr and then slowly warmed to room temperature. The precipitated silver bromide was filtered off with suction and washed with carbon tetrachloride. The filtrate was washed with 2 *N* potassium hydroxide and with water and then dried with calcium chloride. The solvent was removed, using column 6, and the residue from this operation was distilled through a 1.2- by 25-cm Hempel column packed with glass helices.

This reaction is peculiar in that an occasional run failed to yield cyclobutyl bromide. It was noted in the successful runs that during the warming-up period of the bromination step, there was a sharp rise in temperature at about -10° C. This break was not evident in runs in which no yield was obtained. The average yield on the successful runs was 43 percent.

The crude cyclobutyl-bromide samples were combined, washed with water, dried with sodium carbonate, and distilled in column 19. A total of 754 g of purified cyclobutyl bromide was obtained.

(d) *Cyclobutane*. To 48.6 g (2 moles) of magnesium turnings were added 100 ml of dibutyl ether and 6.7 g cyclobutyl bromide. The flask was warmed to 60° C in a water bath until the reaction started. To

this was added over a period of 3 hr 264 g (1.96 moles) of cyclobutyl bromide in 1,250 ml of dibutyl ether. The mixture was stirred for 1¼ hr at 55° to 60° C, after which it was cooled with ice, and 460 ml of *n*-butyl alcohol added slowly. When the addition was complete, the temperature of the mixture was raised slowly until reflux temperature was reached. The escaping gas was passed through the water condenser, an 85-percent sulfuric-acid wash, a 5-percent potassium-hydroxide wash, and a calcium-chloride drying tower, and condensed into a receiver at -30° C. The reaction vessel and purification train were flushed out with dry nitrogen. The yield of cyclobutane in this step was 94 g (84 percent).

From three runs there was obtained a total of 252 g of cyclobutane (about 85-percent yield). The combined samples were fractionated through column 18 and sealed in vacuum [10].

#### 4.8. 2-Pentene

This olefin was prepared by the dehydration of 3-pentanol, obtained by fractionation of a commercial alcohol mixture (see sec. 4.3). A total of 3,080 ml of purified 3-pentanol was passed over the alumina at 300° to 320° C. There was obtained 2,850 ml of organic material and 438 ml of water. The amount dehydrated, based on water recovered, was 86 percent. The organic layer was washed with water, dried over anhydrous sodium carbonate, and distilled in column 19. The center cut was selected for measurement of physical properties and purity shown in table 2 for this compound.

#### 4.9. *trans*-2-Hexene

This compound was prepared by reduction of 2-hexyne with sodium in liquid ammonia. The 2-hexyne was prepared by alkylation of acetylene, and its synthesis is described in a previous paper [12]. The reduction yielded *trans*-2-hexene almost exclusively, in 69-percent yield.

To 10 kg of liquid ammonia (200 g/mole of reactant) in the 10-gal stainless-steel kettle was added with stirring 1,220 g (53 g-atoms) of sodium. No violent exothermic reaction was evident; the sodium dissolved and colored the ammonia a deep blue. The 2-hexyne (1,917 g, 23 moles) was then added as rapidly as the condenser capacity permitted. The solution was allowed to stir for ½ hr after all the material was added, then 6 lb of solid ammonium chloride (50.5 moles) was added in portions to destroy the sodium amide formed. The contents of the pot were stirred for 15 min, after which 5-gal of water was slowly added with stirring. After the layers settled, the organic layer was washed three times with water and dried over anhydrous sodium carbonate.

Distillation of the organic layer on still 19 yielded a 2,000-ml fraction boiling 67° to 69° C (yield 69 percent). The physical constants measured on a center cut of the final distillation are reported in table 2.

#### 4.10. *trans*-3-Hexene

This compound was prepared by reduction of 3-hexyne with sodium in liquid ammonia, as described in section 4.9 for *trans*-2-hexene. For this preparation there was used 8 kg of liquid ammonia, 1,143 g of sodium (50 g-atoms), 1,904 g (23.2 moles) of 3-hexyne, and 2.8 kg (52 moles) of ammonium chloride. The dried organic layer from this run was distilled in column 19 to give 1,608 g (19.2 moles) of product, bp 67° to 68° C. This corresponds to 82-percent yield. The physical properties measured on a middle cut of this compound are given in table 2.

#### 4.11. 1-Octene

This compound was obtained in high purity by careful fractionation of commercial 1-octene. Distillation of 4,000 ml of the crude olefin on column 19 gave 3,500 ml of 1-octene with the properties listed in table 2. A portion of the purified 1-octene was hydrogenated to yield *n*-octane (see sec. 4.1).

#### 4.12. Propadiene

This diolefin was made from the reaction of zinc with 2,3-dichloro-1-propene in methylcellosolve. When this dechlorination was attempted in ethanol [9], no reaction took place.

To a 3-liter flask equipped with stirrer, addition vessel and reflux condenser was added 300 g of zinc dust and 1,000 ml of methylcellosolve. To this mixture at its boiling point (135° C) was added dropwise 325 g (3 moles) of 2,3-dichloro-1-propene. There was an immediate reaction and sufficient evolution of heat to maintain the mixture at its boiling point with the heating mantle removed. The evolved gases were collected in a flask cooled to -78° C. The yield from three such runs was 180 g (50-percent yield). The product was dissolved in 500 ml of *n*-pentane and distilled in column 19. The fraction boiling at -34.5° C was reserved for measurements of the physical properties listed in table 2.

#### 4.13. 2,3-Pentadiene

This compound was obtained by fractional distillation of a sample obtained from a commercial source.

Distillation of 3,000 ml in column 19 yielded a middle cut of 2,200 ml, bp 48° to 49° C. The properties of this material are reported in table 2.

#### 4.14. 2-Methyl-1,3-Pentadiene

This diolefin was prepared from the dehydration of 4-methyl-2-pentene-4-ol.

To prepare the starting material (ethyl crotonate) for this synthesis, a mixture of 5,326 g (62 moles) of crotonic acid, 18.5 liters of 95-percent ethanol, and 172 ml of concentrated sulfuric acid was heated at 95° C in the glass-lined kettle for 8.5 hr. After the mixture had cooled, the contents of the kettle were diluted with 34 liters of water; the organic layer was

washed with sodium carbonate solution and then dried over anhydrous sodium carbonate. Distillation of this crude gave 3.47 kg of ethyl crotonate, bp 137° to 137.5° C, yield 50 percent.

The ethyl crotonate (3.47 kg, 30 moles) was reacted for 2 days at reflux temperature with methylmagnesium bromide made from 7.5 kg of methyl bromide (79 moles) and 1.92 kg of magnesium (79 g-atoms) in 24 liters of ether. At the end of this time, 3 gal of water was added, the ether layer siphoned, washed once with water, and dried over sodium carbonate. The sludge was treated with 11 gal of water containing 9.5 kg of ammonium chloride; the resulting organic layer was washed until neutral to litmus and added to the main batch. The combined ether solution was distilled at atmospheric pressure on column 21. After the ether was stripped, dehydration of the carbinol started at a head temperature of 65° C. When the distillate temperature continued to rise and reached 78° C, the column was placed on total reflux until the temperature fell to 65° C; the takeoff was then continued until a head temperature of 78° C was reached. At this point the column was placed on total reflux again. The operation of the still in this manner between the head temperatures of 65° to 78° C resulted in the dehydration of the carbinol and distillation of the diolefin. About 2 liters of crude diolefin boiling 65° to 78° C was obtained. This material was dried and redistilled in column 18 to obtain 1,710 ml of material boiling 74° to 77° C. For the final pure material needed for this work, the 74° to 77° fraction was redistilled on column 19 under an atmosphere of nitrogen. A center cut was then bottled in vacuum.

The physical constants measured on this compound are listed in table 2. The extremely narrow boiling range of the center-cut sample (0.011 deg C) indicates this material to be of high purity. Chemical tests were used to establish the identity of this diolefin. Treatment with maleic anhydride according to the method of Bachman and Goebel [2] gave a 98-percent yield of 3, 5-dimethyl- $\Delta^4$  tetrahydrophthalic anhydride, mp 57° C. Oxidation of the diolefin with potassium permanganate [2] did not yield acetone, which would arise from the presence of isomeric 4-methyl-1,3-pentadiene, a compound that could be formed in the dehydration process and would be inseparable by ordinary fractional distillation.

#### 4.15. 1,5-Hexadiene

This compound was prepared by the reaction of allyl chloride with magnesium [14]. Two identical 200-mole runs were made in the 50-gal stainless-steel reactor, in each of which 15.2 kg (200 moles) of allyl chloride, 2.82 kg (116 moles) of magnesium, and 60 liters of ether were used. The combined product, after distillation on column 11 (bp 56° to 63° C), amounted to 11.31 kg (138 moles), yield 69 percent. A 2,000-ml portion of the crude hydrocarbon was redistilled on column 19 at a reflux ratio of 100 to 1, under nitrogen, to obtain a pure sample for the determination of the physical properties.

#### 4.16. 2,5-Dimethyl-1,5-Hexadiene

This compound was prepared by the reaction of methallyl chloride with magnesium.

To the stainless-steel kettle was added 778 g (32 g-atoms) of magnesium and about 4 liters of ether. About 200 ml of methallyl chloride was then added, along with a few crystals of iodine to start the reaction. The remainder of the ether (14 liters) was added when the reaction was well under way, following which the addition of the remaining methallyl chloride (total 6.0 kg, 65 moles) was accomplished in 1 hr. The mixture was allowed to stand over night, and the product recovered in the usual way. Distillation on still 6 yielded 2.94 kg of 2,5-dimethyl-1,5-hexadiene, yield 75 percent.

#### 5. Conclusions

Four paraffins, 6 olefins, 5 diolefins, and 3 alicyclic hydrocarbons have been prepared in high states of purity for use in jet-fuel researches. The details of the syntheses and the purification process are given, along with the physical properties measured on the hydrocarbons and their intermediates.

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